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Project Summary

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Organic and Organotin Compounds Leached from PVC and CPVC Pipe

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The primary objective of this research program was to determine whether or not organic forms of tin existed in potable water samples after contact with either polyvinyl chloride (PCV) or chlorinated polyvinyl chloride (CPVC) pipe containing organotin heat stabilizers. Analytical techniques to identify and quantitate organotin compounds at concentrations below one part per billion (ppb) were explored and refined. Four test protocols were used to simulate the extraction process. First, during method development, fragmented pipe samples were digested with extractant water in order to obtain high surface-to-volume ratios, resulting in higher organotin concentrations than would be encountered in the field. Second, extractant water was continuously pumped through an 8.9-meter rectangular closed loop of one-inch internal diameter pipe having an inner surface area of 0.71 m^2 (1100 in^2), maintained at constant temperature. This system was used to provide sequential samples over a 22-day period, during which time the extractant water was completely removed for analysis and replaced at two- to four-day intervals. Third, a miniature pipe system attached to a laboratory faucet was used primarily to study the fate of the solvents incorporated in cements used to join segments of pipe. Fourth, incubation of short lengths of pipe with extractant water served as a convenient method to study changes in leach rates as experimental parameters such as pH were varied.

Commercial pipe samples stabilized with dialkyltin-bis-isooctylthioglycolate compounds were tested. The extractant water was prepared using doubly-distilled water and had hardness, buffer, and chlorine contents similar to that of "Standard" extractant water recommended by the National Sanitation Foundation in its February 1977 Standard 14.

Organotin analysis at these very low levels utilized hydride derivatization, followed by collection of the hydrides on glass bead or OV-1 traps immersed in liquid nitrogen, and detection of tin by atomic absorption spectrophotometry as each hydride eluted sequentially from the trap after the liquid nitrogen was removed. The exact organotin species from which these hydrides arose were not identified, although there was evidence that they existed in ionic form in the extractant water. No evidence of the sulfur-containing part of the stabilizer was found in the extractant water.

The results showed that alkyltin species were extracted from the tested PVC and CPVC pipes by water. The amount of dimethyltin (as the dichloride) leached from PVC into pH 5 extractant water at 37°C was 35 ppb for day one, and decreased from

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approximately 3.0 to 0.25 ppb per 24 hours, in a biphasic manner, from days 2 through 22. The amount of dibutyltin (as the dichloride) leached from CPVC into pH 5 extractant water at 72°C was 2.6 ppb for day one, and decreased from 1.0 to 0.03 ppb per 24 hours, again in a biphasic manner, from days 2 through 21.

Volatile organic solvents (methyl ethyl ketone, tetrahydrofuran, and cyclohexanone were monitored) used in the sealing cements applied to PVC and CPVC pipe joints continued to leach into water supplies for more than 14 days using the miniature pipe system. The quantities ranged from 10 ppm to 10 ppb during the 15 days of sampling.

Sufficient toxicological data are not available to assess the health significance of the very low levels of organotin and cement solvent chemicals found in this study.

This Project Summary was developed by EPA's Health Effects Research Laboratory, Cincinnati, Ohio, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Approximately 800,000 metric tons of polyvinyl chloride (PVC) and co-polymer were produced for pipe and conduit applications in 1977. A portion of this was used in potable water supply systems because of cost and handling advantages over other materials, mainly metals. Use of PVC and chlorinated polyvinyl chloride (CPVC) pipe for potable water raises the question of whether chemicals of a toxic nature diffuse from the pipe into the water supply, and if so, in what quantities. Organotin compounds used as thermal stabilizers in PVC and CPVC pipe formulations are of particular concern if leached, due to their toxicities.

The types of PVC and CPVC used for pipe are rigid materials with little or no plasticizer. They contain compounds such as thermal stabilizers, lubricants, fungicides, fillers, and pigments to aid in processing and prolonging useful life. PVC undergoes complete dehydrochlorination at 300°C, and partial dehydrochlorination at lower temperatures. Thus, a thermal stabilizer must be added to prevent undue degradation of the material during processing. The presence of hydrogen chloride, or the chloride radical, accelerates the decomposition of PVC and CPVC. An important function of a thermal stabilizer is to react with any chloride formed during processing to eliminate it. Stabilizers used with PVC and CPVC in the United States are organometallic salts of tin, calcium, zinc, calcium-zinc, and antimony. Organotin compounds are the most widely used for stabilizing PVC and CPVC potable water pipe. Specific compounds used include methyl-, butyl-, and octyltin esters, particularly of lauric, maleic, and thioglycolic acids. Nine manufacturers have organotin stabilizers accepted by the National Sanitation Foundation (NSF) for use in PVC and CPVC potable water pipe formulations. Organotin stabilizers are used in the range of 0.3 to 1.5 parts per 100 parts resin for PVC pipe and fittings, and in the range of 1.5 to 3.5 parts per 100 parts resin for CPVC pipe and fittings.

Whenever a liquid and solid phase are in contact, there is opportunity for components of the liquid phase to plate out onto the solid, and for components of the solid to be leached into the liquid phase. It is quite possible that potable water could leach some compounds from PVC and CPVC pipes, particularly additives that are mixed with the polymer and not chemically reacted with it. Factors influencing the leaching process include pH, temperature, ionic composition of the water, exposed surface area and surface porosity of the pipe material, water solubility of the polymer additives, the ability of these additives to migrate from within the pipe to the surface, and the reactivity of the additives with each other and with the polymer. Organotin compounds theoretically react with the polymer during stabilization so that only their reaction products are available for leaching, in the form of alkyltin chlorides. However, excess stabilizer is usually present in the pipe.

The primary objective of this research was to determine whether or not organotin compounds were introduced into potable water when using PVC or CPVC pipe containing organotin compounds as stabilizers. A secondary objective was to determine the quantities of other selected organic compounds which might be leached from these pipe systems into the water supply. The approach used was to first establish analytical methodology capable of determining the extracted chemicals present at very low levels, and then to incorporate that methodology in a system to quantify the organotins and other compounds in water supplies after contact with PVC and CPVC pipe. The results obtained are a necessary component of the data needed by toxicologists to determine whether or not the use of plastic pipe for potable water distribution presents a health hazard.

Materials and Instrumentation

As a result of a letter to compounders, pipe fabricators, and manufacturers of tin stailizers, we received 17 pipe samples from eight manufacturers and six resin samples from which some of the pipe samples were formulated. Eight stabilizer samples were received. There were only two negative responses, and 19 manufacturers failed to respond.

Two of the pipe samples were used in pipe-loop experiments. The two samples chosen were representative of widely-used PVC and CPVC pipe compounds. They incorporated primarily dimethyltin- and dibutyltin-bis-isooctylthioglycolate stabilizers, respectively, although stablizer formulations may contain mixtures of alkyltin isooctylthioglycolates. In fairness to manufacturers, and in accordance with our letter requesting samples, all pipe and stabilizer samples are referred to by code.

PCV and CPVC Schedule 80 gray fittings were used in joining the PVC and CPVC loops, respectivley. These fittings met NSF standards. Pieces to be joined were cleaned using a commercial cleaner-primer containing 2-butanone and cyclohexanone. The PVC loop was assembled using a commercial solvent cement containing tetrahydrofuran, 2-butanone, cyclohexanone, N, N-dimethylformamide, and dissolved PVC resin. The CPVC loop was assembled using a similar product containing tetrahydrofuran, 2-butanone, cyclohexanone, and dissolved CPVC resin. The cleaner and cements were purchased locally and met NSF and American Society for Testing and Materials standards. Solvent cement and pipe samples were analyzed by emission spectroscopy prior to use to establish that they contained tin stabilizers.

Organotin reference compounds were purchased from: K & K Rare and Fine Chemicals, Life Science Division of ICN Pharmaceuticals, Inc., Plainview, New York; Alfa Division, Ventron Corporation, Danvers, Massachusetts; Eastman Organic Chemicals, Rochester, New York; and the National Bureau of

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Standards, Washington, D.C. All were used as received, with the exception of dibutyltin dichloride which was recrystallized from hexane prior to use. Methyltin trichloride was the only compound having major impurities. Minor impurities totaling <2% (w/w) were often detected by gas chromatography, and all of the organotin chlorides analyzed by mass spectrometry had detectable organotin bromide contamination. The five compounds used in preparation of quantitative standards for this study had no detectable (>1% w/w) impurities. Both samples of dibutyltin-bis-(2-ethylhexanoate) had certified tin contents, but there was no assurance that all the tin existed in the organic form. There is a general lack of certified organotin reference compounds.

Aqueous solutions of alkyltin halides in the <0.1 - 10 ppm range were prepared fresh daily by serial dilution of 1000-ppm stock solutions. Water was used as solvent for the methyltin halide stock solutions, while acetone or 95% (v/v) ethanol was used as solvent for stock solutions of the other alkyltin halides. Aqueous standards of organotin compounds have often been prepared by dilution of high-concentration stock solutions in ethanol, acetone, or other water-miscible solvent. There was considerable potential for solvent-induced transformations of the original organotin compound to occur with this method of standard preparation. These transformations generally did not hinder the analysis of alkytin species, as the tin-carbon bond was quite stable. These transformations did, however, preclude analysis of the anionic portion of the compound.

Aqueous standard solutions of tetrahydrofuran (Fisher T-397), and methyl ethyl ketone (Fisher M-209) were prepared by serial dilution of an aqueous stock solution containing 100 μL of each chemical per 100 mL of solution. Cyclohexanone (Baker G032) standard solutions were prepared by direct injection of microliter quantities of solvent into water. None of these compounds had detectable (>1% w/v) impurities when analyzed by gas chromatography.

The extractant water composition was similar to that recommended in the February 1977 National Sanitation Foundation Standard 14. Each liter contained 111 mg calcium chloride (Matheson Coleman & Bell CX170) with hardness equivalent to 100 mg calcium carbonate per liter, 84 mg sodium bicarbonate (Matheson Coleman & Bell SX0320) as buffer, and 1.0 mg of chlorine (0.5 mL of a stock 2 g chlorine per liter solution, prepared by adding 7.65 mL of Chlorox, a commercial 5.25% (w/v) solution of sodium hypochlorite, to 200 mL of water). A pH of approximately 5 was obtained by bubbling the solution with carbon dioxide (Linde Bone Dry grade).

A Jarrell-Ash JA 82-270 atomic absorption unit with a Jarrell-Ash FLA-10 Flameless Atomizer was used for both flameless and hydride-generation analyses. A Hewlett-Packard 5730-series gas chromatograph with flame ionization detector and a Hewlett-Packard 3380A integrator were used. All columns were 4-mm internal diameter. The mass spectrometer used in this study was an Associated Electrical Industries MS-30, a double-beam, double-focusing magnetic sector instrument. It was interfaced to a Pye series 104 gas chromatograph via a silicone membrane separator, and coupled to an Associated Electrical Industries DS-30 data system.

Experimental Procedures

Analytical Methods

Two closed-system hydride generation techniques for the detection and quantitation of alkyltin species in environmental samples have been proposed. Braman developed a detector which measured SnH-band emission as the sample was passed through a hydrogen-rich hydrogen-air flame. Hodge developed a method using a hydrogen-rich quartz-tube burner for the atomic absorption analysis of alkyltin hydrides. The applicability of the hydride-generation methods of Hodge and Braman to the analysis of both potable water, and water extracts of plastic pipe intended for potable water transport was thoroughly investigated. Our apparatus had only minor dimensional differences from that used by Hodge.

The hydride generator was a standard 125-mL gas washing bottle to which a septum port for addition of sodium borohydride was added 1 1/2 - 2 inches above the base. The sample was purged with helium to volatilize any hydrides formed and to transfer them efficiently to a trap. The hydride trap consisted of a 20-cm, 4-mm internal diameter glass U-tube packed with 12 cm of 60-70 mesh glass beads with glass wool plugs. This trap was immersed in liquid nitrogen to collect hydrides purged from the hydride generator. The liquid nitrogen was then removed and the trap allowed to warm to room temperature to release the trapped hydrides according to their boiling points. The trap had to be immersed in an ~80°C water bath in order to release tributyltin hydride. The hydride burner consisted of a small Vycor tube positioned in the atomic absorption spectophotometer so that radiation from the hollow cathode lamp passed down the length of the tube. At the midpoint of this tube, air plus helium and sample entered through lines at the front, and hydrogen entered through a line at the rear. These gases mixed at the center of the tube and travelled to its ends, where they were burned in small flames to produce atomic tin which was then quantitatively determined by the magnitude of its absorbance at 224.6, 235.5, or 286.3nm.

Investigation of alternative packing materials for the hydride trap was conducted to improve the separation of organotin hydrides. The use of 18 cm of 10% (w/w) OV-1 on 80/100 mesh Gas-Chrom Q improved separation of methyltin hydrides. After the methyltins eluted, the trap was heated to 145°C to elute the di- and tributyltin hydrides.

Both standard calibration curves and the method of standard additions were used with the hydride-generation atomic absorption technique. Calibration curves were linear over an approximately 20-fold concentration range which varied with the instrument gain. The lowest range used in this work was 0.05 - 1.0 ppb. Results of triplicate analyses at the same organotin concentration in distilled water generally varied by less than 10%. Due to suspected matrix effects, the method of standard additions was selected for quantitative organotin analysis. Duplicate or triplicate analyses of the sample and each addition were performed. Standard aqueous organotin solutions for addition were prepared by serial dilution of an ethanol stock solution.

Grignard alkylation is one of the classic reactions of organic synthesis, involving addition of an alkyl group to a compound through an alkylmagnesium halide intermediate. Grignard butylation and methylation were applied by Meinema to produce tetraalkyltin compounds from various undefined alkyltin species in the aqueous environment. The reaction worked especially well for alkyltin halides, which were used to prepare tetraalkyltin standards. Other alkyltin compounds should react directly,

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or after addition of acid since tin bonds with elements other than carbon are easily cleaved.

Although initial analyses of butylated water extracts of PVC and CPVC pipe showed considerable promise, they also suffered from the disadvantage that tetrabutyltin derived from inorganic tin could not be distinguished from tetrabutyl tin derived from butyltin stabilizer. Since the use of pentyltin compounds as stabilizers had not been reported, we prepared pentyltin derivatives instead of butyltin derivatives.

An interfering gas chromatograph peak coeluted with the dibutyltin derivative due to a derivatization by-product of the complexing agent, tropolone. To overcome this problem, a two-step extraction was developed. First, an extraction of a hydrobromic acid-acidified water sample with benzene was used to recover dibutyltin and tributyltin species. The acidified water sample was then extracted with benzene containing 0.05% (w/v) tropolone to recover the monobutyltin and inorganic tin species. The two extracts were derivatized separately, using n-pentylmagnesium bromide (1.5 - 2.5 M in ether, Alfa 87296). The derivatives were analyzed by gas chromatography on a column of 10% (w/w) OV-1 on Gas-Chrom Q.

The limit of detection of the Grignard alkylation technique, corresponding to approximately 1.5 - 3 ug alkyltin species in 1 L water, was not as low as that of the hydride-generation atomic absorption method. However, the Grignard alkylation method provided a sample suitable for analysis by mass spectrometry, allowing verification of the presence of alkyltin species.

Extraction Experiments

Fragmented pipe samples were used to provide a large surface area for determining what compounds were water extractable. One- to two-inch internal diameter pipe was sawed into four- to six-inch lengths and cleaned before (and after) fragmenting. The plastic was fragmented by freezing it in liquid nitrogen, wrapping it in clean duck canvas, and hammering on a hard supporting surface. This process resulted in irregularly-shaped, 0.35-cm thick pieces, 0.25 to 1.5 cm in length and width. About 400 grams of pipe fragments were placed in a 500-mL Pyrex bottle which was then filled with extractant water (approximately 200 mL). A 5-cc air space was left for the expansion of bottle contents on heating. Each bottle was sealed with a ground glass stopper. A blank, consisting of a bottle filled only with extractant water, was run with each set of fragmented pipe samples.

The basic component of the pipe-loop system was a 1.71-m (5.6-foot) by 2.74-m (9-foot) rectangular closed loop of one-inch internal diameter pipe having an inner surface area of 0.71 m^2 (1100 in^2).The loop of 8.9-m (29.2-foot) total length was formed using conventional NSF-accepted elbows and solvent cement as described in the Materials and Instrumentation section. Test water was circulated in the loop by a centrifugal pump (Process Controls Co., Livonia, MI 48152. Pump: Dayton Model 6K122. Pump head: Liquiflo, Warren, NJ 07060) having only wetted stainless steel and Teflon parts. A galvanized pipe loop of the same length and internal diameter was mounted adjacent to the plastic loop and utilized an identical pump.

Each loop was filled and drained by means of a fill tube that fit directly into an access port at the bottom of the pump head. This port was the lowest point in the system. Another port at the top of the pump head, the highest point in the system, served as a vent and an overflow indicator to signal when the loop was full. Extractant water volumes required to fill the control, PVC and CPVC loops were 4.8, 4.1, and 3.9 liters, respectively. Volume differences probably reflect variations in the nominal internal diameters of the pipes. The loops were housed in a controlled-temperature heated test chamber, built of sheets of polystyrene insulation. Heating elements were incorporated to heat the chamber to 37°C when testing the PVC loop and 72°C when testing the CPVC loop.

A report by Wang and Bricker stating that cement solvents could be detected in water six to eight months after installation of a PVC pipe system, led us to set up a miniature pipe system to address this problem specifically. The system was attached to a laboratory faucet and was assembled using a galvanized fitting, two gray PVC connectors, four gray PVC elbows, three 0.102-m (4-inch) pieces of PVC sample #9A, and two 0.40-m (16-inch) pieces of PVC sample #14A. The last component of the system was a brass gate valve positioned over a sink. There were 10 solvent-cemented joints in this 1.22-m (48-inch) miniature pipe system. The inner surface area of the plastic was approximately 0.1 m^2 (151 in^2), and the volume of the system was approximately 600 mL. The NSF-accepted solvent cleaner-primer and solvent cement, described in the Materials and Instrumentation section, were used.

When the gate valve was closed, water resided in the system under normal line pressure. When the water was turned off at the faucet, the gate valve could be opened and water from the system collected in a Pyrex bottle, undiluted for an analysis, after a known residence time. Samples were taken periodically over a 2-week period after 4- to 20-hour residence times in the system at normal line pressure. At all other times, water flowed through the system at approximately 4 liters per minute. Water to serve as a blank could be drawn from the same line using the faucet at the sink.

In the pipe incubation method, one-inch PVC or CPVC pipe was cut into 2-inch lengths, placed in a wide-mouth Pyrex jar, and covered with extractant water with no headspace in the container. The amount of pipe and water was such that there was 4mL of water per square inch of exposed pipe surface, as recommended by NSF in their standard testing protocol. Incubation was carried out at 25°C with continuous shaking for periods of time up to 168 hours. The water was removed for analysis and replaced with fresh water every 24 hours, unlike the pipe loop system where the water was removed for analysis and replaced at 48- to 72-hour intervals.

Results and Discussion

Analysis of Pipe Fragment Extracts

A fragmented sample of CPVC #6 was digested in pH 5.7 extractant water for 72 hours at 82 ± 3°C and the resulting water sample was reacted with sodium borohydride. The pH of the extractant water, adjusted by bubbling carbon dioxide through it, varied during initial tests as bubbling rates and times were explored. The 82°C temperature was the maximum reasonable temperature for testing CPVC pipe. The extractant water from the CPVC #6 digestion was then extracted with diethyl ether and the concentrated ether extract was analyzed by gas chromatography. The chromatogram, obtained on a 3% (w/w) OV-17 column held at an isothermal temperature of 90°, revealed six peaks,

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none of which appeared in the blank. The sample was reanalyzed by gas chromatography/mass spectrometry. The two major peaks were identified as octanol isomers. No evidence of either tin or chlorine was found in any peak.

Pipe fragment extracts of PVC sample #14A and CPVC sample #14C were analyzed by the Grignard alkylation procedure. The butylated extract of PVC sample #14A contained dibutyldimethyl tin and tributylmethyl tin, indicating the presence of methyltin species in the water. A butylated extract of CPVC #14C contained tetrabutyl tin. A methylated extract of the same sample contained dibutyldimethyl tin, indicating the presence of butyltin species in the water after contact with CPVC pipe. All identifications were confirmed by mass spectrometry.

Miniature Pipe System

The continuous-flow pipe system was set up for collection of water samples for cement solvent analysis. Analysis was performed by direct injection of a 5-μL portion of the water sample onto a gas chromatograph column packed with 1% (w/w) SP-1000 on 60/80 Carbopack B, maintained at an isothermal temperature of 170°C. Standards for tetrahydrofuran, methyl ethyl ketone, and cyclohexanone analysis were prepared by direct injection of known amounts of the solvents dissolved in water.

N, N-dimethylformamide was not analyzed. Cyclohexanone was only detectable at the 1-2 ppm level in Day 1 samples. The only samples in which ppm-quantities of solvents were detected in a flowing system were taken on Day 1. On subsequent days, one sample was taken after a 6-9 hour residence time in the system. Flow was maintained at ~2-4 liters per minute at all other times.

Three conclusions were apparent from this experiment. First, ppm quantities of tetrahydrofuran and methyl ethyl ketone (<0.5 - 5 ppm each), and ppb quantities of methyltin species (0.1 - 0.8 ppb dimethlytin) were detectable more than two weeks after installation of the system and after over 10,000 gallons of water had flowed through the system. Second, there was no doubt that the substances tested could have been detected longer than two weeks. Third, there was the distinct possibility that our building or municipal water supply contained low-ppb levels of organotin species, since blank samples drawn from an adjacent faucet showed three unidentified alkyltins.

Analysis for these same cement solvents was performed on water samples collected from the pipe loop experiments (next section). However, the results from this miniature pipe system were more meaningful in demonstrating the unexpected persistance of the solvents, inasmuch as the amount of water used in the miniature pipe system was orders of magnitude greater than the amount of water used in a pipe loop.

Pipe Loop Experiments

In each experiment a control loop of one-inch internal diameter galvanized pipe, assembled using galvanized fittings, was employed and sampled concurrently to provide blank samples. Only one sample from a control loop had detectable amounts of organotin species, which have been subtracted from the reported results. The pH of the extractant water used to fill each loop was 5.0 ± 0.2.

The first experiment utilized PVC sample #14A pipe, assembled using solvent-cemented PVC elbows and one metal connector. The stabilizer used in formulating this pipe was dimethyltin-bis-isooctylthioglycolate. A total of nine samples were collected from each loop during the exposure period of 21 days and 20 hours. Each loop was filled with extractant water, the water was continuously pumped through the loop for 24- to 96-hour periods, the entire water sample from the loop was drained into a glass carboy, and the loop was refilled with extractant water. Each sample collected from each loop was analyzed for organotin species and for cement solvents on the day it was collected.

The water samples contained small amounts of solid particles, less than 1-millimeter in length and present in two physical forms. Some were opaque and irregular, as though fragmented from the pipe. Others were translucent flakes or spheres, similar in appearance to flakes of dried solvent cement obtained from around the top of the container. Because this particulate matter affected the reproducibility of repeated runs on each sample, the samples were filtered prior to analysis.

Quantitative alkyltin analyses were carried out using hydride-generation atomic absorption and the method of standard additions. Results of organotin analysis of the nine samples from the PVC sample #14A pipe loop are given, in several different forms, in Table 1. Monomethyltin was only found in the sample from the first contact period, where it gave a peak height of about one twentieth that of the dimethyltin. Results for the dimethyltin and trimethyltin species are expressed in terms of their respective chlorides. The ppb/contact time (1-4 days) is given, along with the concentration in ppb standardized to a 24-hour time period and the cumulative amount of each compound, in μg, leached during the course of the test. Statistical information on the precision of analysis, in terms of the mean and standard deviation, is given in the ppb/contact time column. A total of 223.6 ug dimethyltin dichloride and of 71.6 ug trimethyltin chloride leached into the extractant water during this pipe loop experiment.

Results of cement solvent analyses of the nine samples from the PVC sample #14A pipe loop are shown in Figure 1. Cyclohexanone was only detectable in the first five samples (at greater than 1 ppm), but tetrahydrofuran and methyl ethyl ketone were detectable in all nine samples. This again demonstrated the unexpected persistence of these water-soluble chemicals.

The second experiment utilized CPVC sample #14C pipe, assembled using solvent-cemented CPVC elbows and connectors. The stabilizer used in formulating this pipe was primarily dibutyltin-bis-isooctylthioglycolate. Filling, operating, and sampling the loop were performed as described for the PVC pipe loop. A galvanized control loop was tested concurrently. Seven samples were collected from each loop during the 21-day exposure period. The CPVC loop extractant water samples were filtered before analysis to remove the persistent particle contamination.

In the first few analyses of samples from this CPVC loop, an interference eventually attributed to chlorine was encountered in the hydride-generation analyses. After tracing the problem, samples were dechlorinated by adding a stoichiometric amount of sodium thiosulfate as part of the analytical process. However, this did not solve the interference problem completely, in that it was found that the amounts of alkyltin hydrides formed were not proportional to the amounts of sample used. The analytical procedure was changed to work around this problem. The altered procedure involved running all the samples under the same instrumental conditions, using the same amount of sample for each analysis. Likewise, the same volumes of extractant water

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Table 1. *Results of Organotin Analyses of Samples from the PVC Sample #14A Pipe Loop**

Sample Number	Total Elapsed Time, days	Contact Time of Sample, days	Dimethyltin species, as $(CH_3)_2SnCl_2$+			Trimethyltin species, as $(CH_3)_3SnCl$+		
			1	2	3	1	2	3
1	1	1	35. ± 2.0	35.	143.5	13. ± 1.2	13.	53.3
2	3	2	4.8 ± 0.5	2.4	163.2	1.7 ± 0.1	0.85	60.3
3	6	3	1.0 ± 0.2	0.33	167.3	0.21 ± 0.04	0.07	61.2
4	8	2	1.0 ± 0.1	0.50	171.4	0.14 ± 0.01	0.07	61.8
5	10	2	5.6 ± 0.6	2.8	194.4	0.90 ± 0.09	0.45	65.5
6	13	3	3.9 ± 0.6	1.3	210.4	0.75 ± 0.11	0.25	68.6
7	16	3	1.5 ± 0.1	0.50	216.6	0.39 ± 0.01	0.13	70.2
8	20	4	1.0 ± 0.1	0.25	220.7	0.24 ± 0.03	0.06	71.2
9	22	2	0.7 ± 0.1	0.35	223.6	0.10 ± 0.02	0.05	71.6

**The surface area of pipe in contact with extractant water was approximately 1100 in ^{2}. In comparing these results with results of other tests it is imperative to take into account the ratio of exposed pipe surface area to extractant water volume, which in this case was approximately one square inch to 3.7 mL.*

+*Column 1: Results expressed in terms of ppb/contact time; mean ± standard deviation.*
Column 2: Results expressed in terms of ppb/24 hours; mean.
Column 3: Results expressed in terms of cumulative µg leached during the 22-day study; mean.

containing known amounts of the alkyltin chlorides (dimethyl, trimethyl, monobutyl, and dibutyl) were run as standards. One milliliter of 0.07% (w/v) sodium thiosulfate solution was added to both samples and standards to neutralize the chlorine effect.

The contact period and analytical results are listed in Table 2. A total of 35.7 µg dibutyltin dichloride leached into the extractant water during this pipe loop study. Dimethyltin dichloride and trimethyltin chloride were also observed in some of the CPVC pipe loop water samples.

Water samples from the CPVC sample #14C pipe loop were also analyzed for three of the solvents introduced by the solvent cement. Results (Figure 2) were about the same as in the PVC experiment, although the cements used were slightly different for the two polymers.

Pipe Incubation Results

Organotin chloride concentrations in water samples analyzed in the independent pipe incubation study of CPCV sample #4 were remarkably similar to those in the CPVC sample #14C pipe loop study. A rapid initial decrease in alkyltins was noted, followed by a secondary increase and subsequent decrease. The same species (monobutyl-, dibutyl-, dimethyl-, and trimethyltin) were found. The reason for the secondary maximum organotin concentration may be understood more fully after completion of the independent pipe incubation studies.

Quality Assurance Testing

This project was conducted in accordance with EPA Quality Assurance requirements. Quality assurance samples were analyzed along with the PVC sample #14A pipe loop samples for both methyltin species and for cement solvents. Retention times and peak heights produced by four aliquots of a working standard containing the three butyltin chlorides, analyzed successively by the hydride-generation atomic absorption procedure, varied by less than 10%.

Conclusions and Recommendations

1. Alkyltin species were extractable from PVC and CPVC pipes by water. The amount of dimethyltin (as the dichloride) leached from PVC into pH 5 extractant water at 37°C was 35 ppb for day one, and decreased from approximately 3.0 to 0.25 ppb per 24 hours in a biphasic manner from days 2 through 22. The amount of dibutyltin (as the dichloride) leached from CPVC into pH 5 extractant water at 72°C was 2.6 ppb for day one, and decreased from 1.0 to 0.03 ppb per 24 hours, again in a biphasic manner, from days 2 through 21. Both results were obtained when pumping extractant water continually through an 8.9-meter rectangular closed loop of one-inch internal diameter pipe having an inner surface area of 0.71 m^2 (1100 in^2), over a 22-day period, during which time the water was completely removed for analysis and replaced at two- to four-day intervals.
   a. The exact organotin compounds from which these alkytin species arose were indefinite, although there was evidence that they existed in ionic form in the extractant water.
   b. No evidence of the sulfur-containing part of the stabilizer was found in the extractant water.
   c. The dynamics of the extraction process were not fully resolved, but the rate of decrease at the end of 21 days indicated that detectable amounts (0.005 ppb per 24 hours contact time) of organotin species would be present for long periods of time under normal service.
   d. Experiments should be performed to determine leaching rates at other pH and temperature conditions. Testing should be carried out over longer time periods (6-12 months) to determine whether or not extraction of organotin species is a continuing process.
   e. Future studies should be directed toward determining whether these levels present a human health hazard. Therefore, further analytical work, as outlined in (d), should be performed in conjunction with toxicity testing of the extractant water samples, or equivalent synthetic samples at the low-ppb level.

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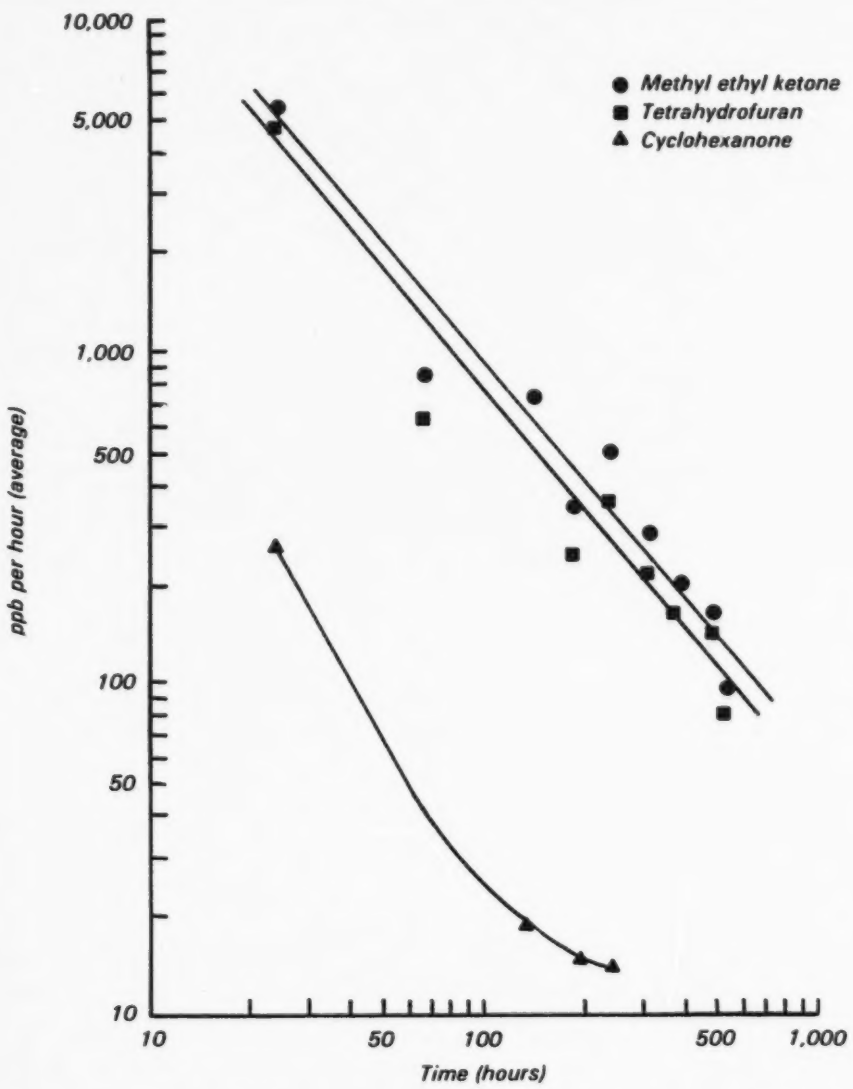

Figure 1. *Standardized cement solvent concentrations observed in PVC sample #14A pipe loop water samples.*

2. Volatile organic solvents (methyl ethyl ketone, tetrahydrofuran, and cyclohexanone were monitored), used in the sealing cements applied to PVC and CPVC pipe joints, continued to leach into water supplies for more than 14 days using the miniature pipe system. The quantities ranged from 10 ppm to 10 ppb during the 15 days of sampling.
3. The hydride-generation methods of Hodge, Braman, and others permitted organotin analysis at concentrations below 0.01 ppb.
   a. Matrix effects were encountered using hydride generation. Although the major effect resulted from chlorine in the sample and was overcome by adding sodium thiosulfate to the sample, considerably more work is needed to understand and control more subtle matrix effects. A single analytical procedure may not be suitable for all sample matrices.
4. The Grignard derivatization method was applicable to the organotin species encountered in water extracts of CPVC pipe when the pentyl derivatives were used, rather than the methyl and butyl derivatives recommended by Meinema.
5. Other conventional methods of concentrating, separating, and identifying the organotin compounds of interest did not prove to be readily applicable. These included high-pressure liquid chromatography, ion-pairing chromatography, flameless atomic absorption, and thin-layer chromatography. Mass spectrometry was useful in conjunction with the hydride and Grignard derivatization methods for identification of various constituents.

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Table 2. *Results of Organotin Analyses of Samples from the CPVC #14C Pipe Loop**

Sample Number	Total Elapsed Time, days	Contact Time of Sample, days	Alkyltin species, as $(CH_3)_2SnCl_2^+$			$(CH_3)_3SnCl^+$			$C_4H_9SnCl_3^+$			$(C_4H_9)_2SnCl_2^+$		
			1	2	3	1	2	3	1	2	3	1	2	3
1	1	1	0.61	0.61	2.4	0.30	0.30	1.2	0.63	0.63	2.5	2.6	2.6	10.1
2	3	2	0.34	0.17	3.7	<0.01	<0.01	1.2	0.66	0.33	5.1	2.0	1.0	17.9
3	6	3	0.06	0.02	3.9	—	—		0.39	0.13	6.6	0.84	0.28	21.2
4	10	4	0.12	0.03	4.4	—	—		0.08	0.02	6.9	2.2	0.55	29.8
5	14	4	0.12	0.03	4.9	—	—		—	—		0.80	0.20	32.9
6	17	3	—	—		—	—		—	—		0.60	0.20	35.2
7	21	4	—	—	4.9	—	—	1.2	—	—	6.9	0.12	0.03	35.7

**The surface area of pipe in contact with extractant water was approximately 1100 in^2. In comparing these results with results of other tests it is imperative to take into account the ratio of exposed pipe surface area to extractant water volume, which in this case was approximately one square inch to 3.5 mL.*

\+ *Column 1: Results expressed in terms of ppb/contact time.*
Column 2: Results expressed in terms of ppb/24 hours..
Column 3: Results expressed in terms of cumulative µg leached during the 21-day study.

—Below the detection limit.

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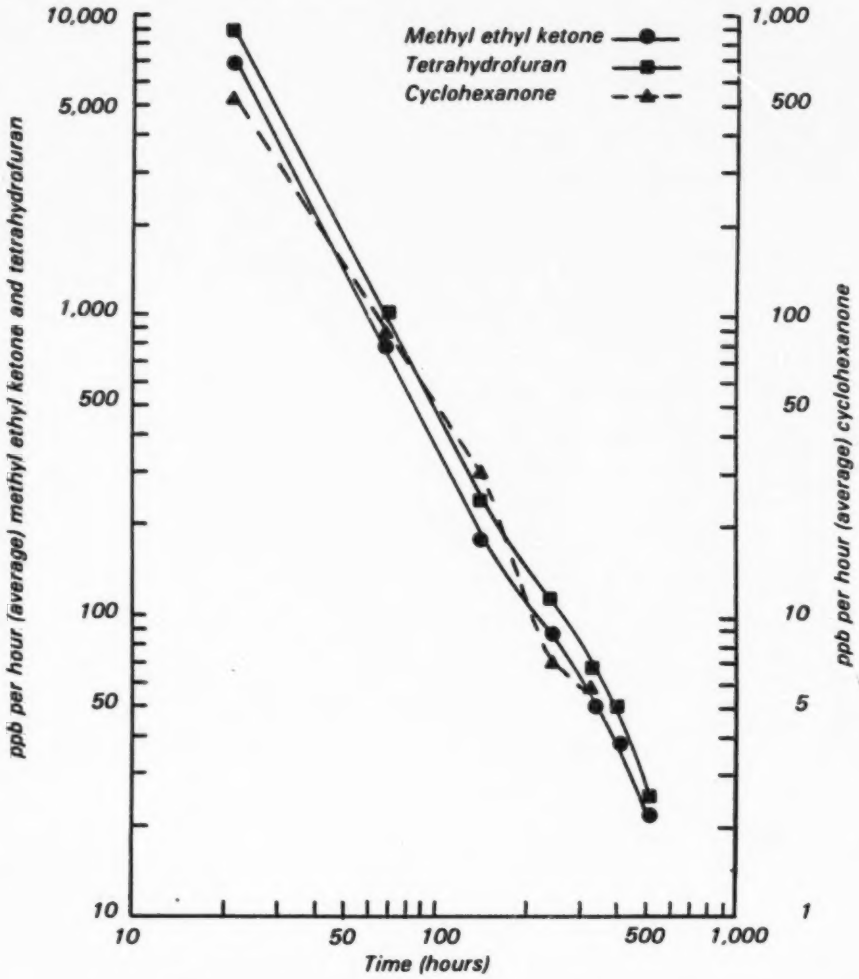

Figure 2. *Standardized cement solvent concentrations observed in CPVC sample #14C pipe loop water samples.*

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***Nancy S. Ulmer** is the EPA Project Officer (see below).*
The complete report, entitled "Organic and Organotin Compounds Leached from PVC and CPVC Pipe," (Order No. PB 82-108 333; Cost: $11.00, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
The EPA Project Officer can be contacted at:
Health Effects Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH 45268

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